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Green Ocean Amazon (GoAmazon) 2014/15: Semi-Volatile Thermal Desorption Aerosol Gas Chromatograph (SVTAG) Field Campaign Report

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Executive Summary

In areas where biogenic emissions are oxidized in the presence of anthropogenic pollutants such as SO_2, NO_x, and black carbon, it has become increasingly apparent that secondary organic aerosol (SOA) formation from biogenic volatile organic compounds (VOCs) is substantially enhanced. Research is urgently needed to elucidate fundamental processes of natural and anthropogenically influenced VOC oxidation and the contribution of these processes to SOA formation. GoAmazon 2014/15 afforded study of the chemical transformations in the region downwind of Manaus, Brazil, where local biogenic VOC emissions are high, and their chemical oxidation can be studied both inside and outside of the urban plume to differentiate the role of anthropogenic influence on secondary aerosol formation during oxidation of these natural VOC emissions. To understand the connection between primary biogenic VOC emissions and their secondary products that form aerosols, we made time-resolved molecular level measurements by deploying a Semi-Volatile Thermal Desorption Aerosol Gas Chromatograph (SV-TAG) and a sequential filter sampler during two intensive operational periods (IOPs) of the GoAmazon 2014/15 field campaign. The SV-TAG measured semi-volatile organic compounds in both the gas and particle phases and the sequential filter sampler collected aerosols on quartz fiber filters in four-hour increments used for offline analysis. SV-TAG employed novel online derivatization that provided chemical speciation of highly oxygenated or functionalized compounds that comprise a substantial fraction of secondary organic aerosols, yet are poorly characterized. It also provided partitioning of these compounds between the vapor and particle phases at sufficient time resolution to define the importance of competing atmospheric processes. These measurements were supported by offline analysis of the filters using two-dimensional gas chromatography (GC x GC) with high-resolution time-of-flight mass spectrometry (HR-TOF-MS) using both electron impact (EI) and soft vacuum ultraviolet (VUV) ionization with derivatization. Speciated chemical data from SV-TAG and filter measurements were used to elucidate the relative importance of potential oxidation pathways by providing detailed information on the product distribution from atmospheric reactions and the quantification of known tracers for various oxidation pathways. Together, these techniques provided unequivocal molecular identification of a wide range of atmospheric organic compounds spanning the volatile, semi-volatile, and non-volatile phases. This level of chemical characterization provided insight into the chemical and physical processes that control the atmospheric oxidation of biogenic VOC and subsequent formation of SOA.

Acronyms and Abbreviations

AMF	ARM Mobile Facility
ARM	Atmospheric Radiation Measurement Climate Research Facility
BVOC	biogenic volatile organic compound
DOE	U.S. Department of Energy
EI	electron impact
GC	gas chromatograph(y)
GoAmazon	Green Ocean Amazon 2014/15
HR-TOF-MS	High-Resolution-Time-of-Flight Mass Spectrometry
INPA	Instituto Nacional de Pesquisas da Amazonia
INPE	Instituto Nacional de Pesquisas Espaciais
IOP	intensive operational period
LBA	Large Scale Biosphere Atmosphere Experiment in Amazonia
LANL	Los Alamos National Laboratory
NSF	National Science Foundation
PI	Principal Investigator
BSOA	Biogenic Secondary Organic Aerosol
SOA	secondary organic aerosol
SV-TAG	Semi-Volatile Thermal Desorption Aerosol Gas Chromatograph
VOC	volatile organic compound
VUV	vacuum ultraviolet

Contents

Figures

1.0 Background

Background information for this campaign is from the campaign website: http://www.seas.harvard.edu/environmental-chemistry/GoAmazon2014/. Additional details describing the development of the campaign including the white paper can also be found there. An excerpt on the background for the deployment:

The deployment site, downwind of the city of Manaus, Brazil (3° 6' 47" S, 60° 1' 31" W) near Manacapuru, is situated so that it experiences the extremes of i) a pristine atmosphere when the Manaus pollution plume meanders and ii) heavy pollution and the interactions of that pollution with the natural environment when the plume regularly intersects the site. The city of Manaus uses high-sulfur oil as its primary source of electricity; the city is also an industrial zone of several million people and has high emissions of soot. Particle number and mass concentrations are 10 to 100 times greater in the pollution plume compared to the times when pristine conditions prevail. The deployment will enable the study of how aerosol and cloud life cycles, including cloud-aerosol-precipitation interactions, are influenced by pollutant outflow from a tropical megacity.

Instrumentation was co-located at the Manacapuru, Brazil U.S. Department of Energy's Atmospheric Radiation Measurement (ARM) Climate Research Facility site during two IOPs: IOP1 wet season February 1–March 30 2014 and IOP2 dry season August 15–October 15 2014. An exhaustive list of collaborating agencies, principal- and co-investigators, as well as additional team members and their affiliations, can be found at the campaign website listed above.

Specifically, we would like to acknowledge support from the U.S. National Science Foundation and the U.S. Department of Energy. We also acknowledge the support from the Central Office of the Large Scale Biosphere Atmosphere Experiment in Amazonia (LBA), the Instituto Nacional de Pesquisas da Amazonia (INPA), the Instituto Nacional de Pesquisas Espaciais (INPE), the Universidade do Estados do Amazonas (UEA), the FAPESP São Paulo Research Foundation, and the Fundação de Amparo à Pesquisa do Estado do Amazona. The work was conducted under 001030/2012-4 and 001262/2012-2 of the Brazilian National Council for Scientific and Technological Development (CNPq).

2.0 Notable Events or Highlights

Notable events include confirmed Manaus plume presence (via aircraft) on March 13 2014 during IOP1 and significant biomass burning events (as indicated by levoglucosan tracer) the nights of September 30–October 2 2014 during IOP2. See timeline of IOP2 levoglucosan in Figure 1 below.

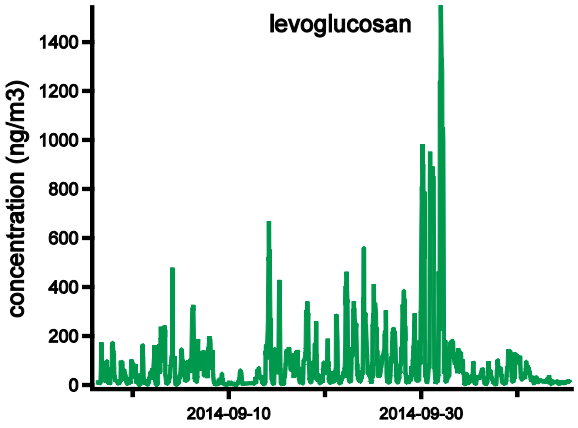

Figure 1. Levoglucosan timeline during GoAmazon 2014/15 IOP2.

3.0 Lessons Learned

Acquisition of chemicals in Brazil unfortunately had a longer lead time than expected in planning. This affected our ability to collect derivatized data on SV-TAG, delaying normal data collection until February 16 2014. Due to the special nature of the derivatizing agent and the longer lead time, future deployments would need to account for this even further in advance, or we should have opted to have it shipped from the United States with the Los Alamos National Laboratory (LANL)/ARM-organized shipment. Key decisions that would affect the site and thereby atmospheric measurements were not always well coordinated between guest instrumentation and AMF operators. Improvements in communication were made between IOPs to resolve this issue.

4.0 Results

We observed 2-methyltetrols, indicators of isoprene oxidation to partition readily between the gas and particle phases (Figure 2). These are the first online partitioning measurements of these and other compounds measured in the Amazon. Sesquiterpenes (Figure 3) were also observed to be in relatively high abundance (~tens of ppt_v) and anti-correlated with ozone. This is also the first time they have been measured with hourly time resolution in the Amazon. Additional BVOCs and tracers were measured and will be included in the ARM Data Archive.

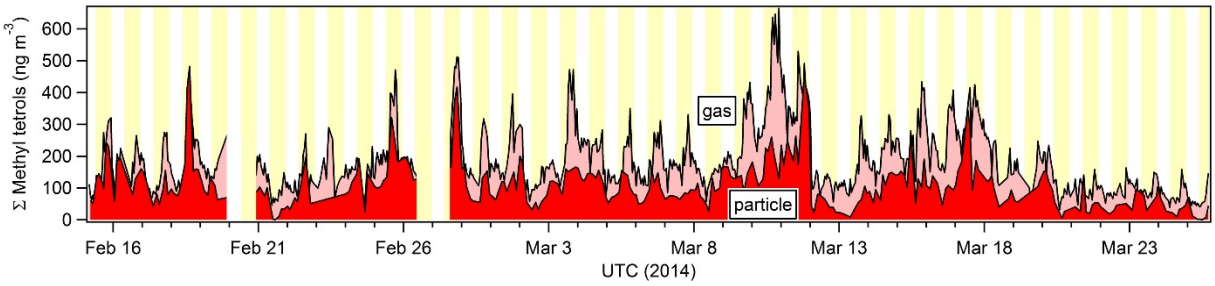

Figure 2. Summed 2-methyltetrols in the gas (pink) and particle (red) phases during IOP1 of GoAmazon 2014/15. Local daylight hours (typically around 6 AM-6 PM LT) indicated by yellow shading.

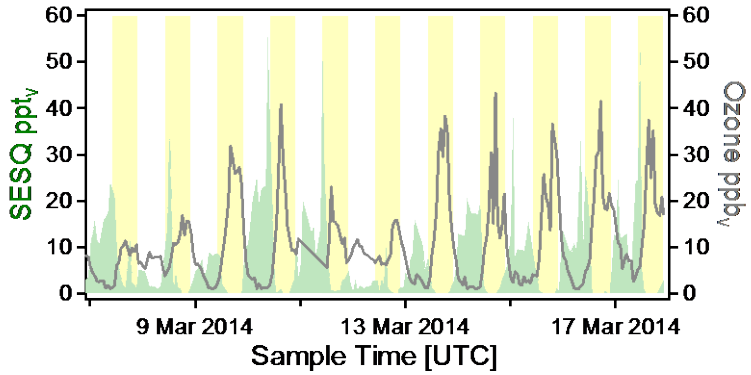

Figure 3. Sesquiterpenes (green) are anti-correlated with ozone (grey). Local daylight hours (typically around 6 AM-6 PM LT) indicated by yellow shading.

Further research opportunities include exploration of the sesquiterpene oxidation products via controlled chamber oxidation experiments and discovery of additional BSOA tracers that will enhance our understanding of the GoAmazon 2014/15 data set. Additional analyses for sesquiterpene oxidation products was funded by U.S. DOE ASR (DE-SC0014040)

5.0 Public Outreach

Campaign web addresses:

1. http://www.seas.harvard.edu/environmental-chemistry/GoAmazon2014/

2. http://campaign.arm.gov/goamazon2014/

6.0 Green Ocean Amazon Publications

6.1 Journal Articles/Manuscripts

1. Isaacman, G, NM Kreisberg, LD Yee, DR Worton, AWH Chan, J Moss, SV Hering, and AH Goldstein. 2014. "Online derivatization for hourly measurements of gas- and particle-phase semi-volatile oxygenated organic compounds by thermal desorption aerosol gas chromatography (SV-TAG)." *Atmospheric Measurement Techniques* 7: 4417-4429, doi:10.5194/amt-7-4417-2014.

Working titles for planned manuscripts:

2. Gas-particle partitioning of biogenic oxidation products in forested environments

3. Observational constraints on terpene oxidation in the Amazon using speciated measurements from SV-TAG

4. Characterizing the chemical complexity of semi-volatile organic compounds from biomass burning in Amazonia

6.2 Meeting Abstracts/Presentations/Posters

1. Wernis, RA, LD Yee, G Isaacman-VanWertz, NM Kreisberg, S de Sá, Y Liu, ST Martin, ML Alexander, BB Palm, W Hu, P Campuzano-Jost, DA Day, JL Jimenez, P Artaxo, J Viegas, A Manzi, R de Souza, SV Hering, and AH Goldstein. "Characterizing the chemical complexity of semi-volatile organic compounds from biomass burning in Amazonia," 05/18/15, GoAmazon 2014 Science Meeting, Cambridge, MA.
2. Isaacman-VanWertz, G, and AH Goldstein. "Factors controlling gas-particle partitioning and formation of secondary organic aerosol from isoprene oxidation," 05/20/15, GoAmazon 2014 Science Meeting, Cambridge, MA.
3. Yee, LD, G Isaacman-VanWertz, RA Wernis, NM Kreisberg, Y Liu, KA McKinney, S de Sá, ST Martin, ML Alexander, BB Palm, W Hu, P Campuzano-Jost, DA Day, JL Jimenez, J Viegas, SR Springston, F Wurm, JF Brito, P Artaxo, A Manzi, LAT Machado, K Longo, MB Oliveira, R de Souza, SV Hering, and AH Goldstein. "Observational constraints on terpene oxidation in the Amazon using speciated measurements from SV-TAG," 05/18/15, GoAmazon 2014 Science Meeting, Cambridge, MA.

4. Isaacman, G, LD Yee, NM Kreisberg, S de Sá, ST Martin, ML Alexander, BB Palm, W Hu, P Campuzano-Jost, DA Day, JL Jimenez, TKV Nguyen, AG Carlton, J Viegas, SR Springston, A Manzi, R de Souza, MB Oliveira, P Artaxo, JF Brito, E Edgerton, K Baumann, SV Hering, and AH Goldstein. "Understanding factors affecting partitioning of oxygenated organics in natural and polluted environments using SV-TAG," 12/17/14, American Geophysical Union, San Francisco, CA

5. Yee, LD, G Isaacman-VanWertz, RA Wernis, NM Kreisberg, Y Liu, KA McKinney, S de Sá, ST Martin, ML Alexander, BB Palm, W Hu, P Campuzano-Jost, DA Day, JL Jimenez, J Viegas, SR Springston, F. Wurm, JF Brito, P Artaxo, A Manzi, LAT Machado, K Longo, MB Oliveira, R de Souza, SV Hering, and AH Goldstein. "Observational constraints on terpene oxidation in the Amazon using speciated measurements from SV-TAG," 12/15/14, American Geophysical Union, San Francisco, CA.

6. Isaacman-VanWertz, G, LD Yee, NM Kreisberg, S de Sá, Y Liu, S Martin, L Alexander, BB Palm, W Hu, P. Campuzano-Jost, DA Day, JL Jimenez, J Viegas, A Manzi, R de Souza, MB Oliveira, P Artaxo, JF Brito, P Misztal, E Edgerton, K Baumann, SV Hering, and AH Goldstein. "Isoprene oxidation products measured by SV-TAG reveal differences in chemistry and partitioning between natural and polluted environments," 09/23/14, International Global Atmospheric Chemistry, Natal, Rio Grande do Norte, Brazil.

7. Yee, LD, G Isaacman-VanWertz, NM Kreisberg, Y Liu, KA McKinney, S de Sá, ST Martin, ML Alexander, BB Palm, W Hu, P Campuzano-Jost, DA Day, JL Jimenez, J Viegas, SR Springston, F Wurm, JF Brito, P Artaxo, A Manzi, LAT Machado, K Longo, MB Oliveira, R de Souza, SV Hering, and AH Goldstein. "Observational constraints on terpene oxidation with and without anthropogenic influence in the Amazon using speciated measurements from SV-TAG," 09/26/14, International Global Atmospheric Chemistry, Natal, Rio Grande do Norte, Brazil.

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